

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 001 082 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

17.05.2000 Bulletin 2000/20

(21) Application number: 99923869.4

(22) Date of filing: 02.06.1999

(51) Int. Cl.⁷: **D21H 17/14, D21H 21/24**

(86) International application number:

PCT/JP99/02947

(87) International publication number:

WO 99/63156 (09.12.1999 Gazette 1999/49)

(84) Designated Contracting States:

DE ES FR GB

(30) Priority: 02.06.1998 JP 15281498

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(54) PAPER BULKING AGENTS

(57) According to the present invention, a bulky sheet can be obtained without reducing the effect of a sizing agent. Thus, an ester compound having the melting point of not more than 100°C selected from (A) an ester compound of a polyhydric alcohol and a fatty acid and (B) an ester compound of a polyhydric alcohol and a fatty acid further including from more than 0 mole to less than 12 moles on the average of C₂₋₄ oxyalkylene groups per 1 mole of the said ester compound is used as a paper bulking promoter.

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Description

Technical Field

- 5 [0001] This invention relates to a paper bulking promoter with which sheets of paper obtained from a pulp feedstock can be bulky without reducing the effect of a sizing agent.

Background Art

- 10 [0002] Recently, there is a desire for high-quality paper, e.g., paper excellent in printability and voluminousness. Since the printability and voluminousness of paper are closely related to the bulkiness thereof, various attempts have been made to improve bulkiness. However pulp recycling is made to be impossible as well as smoothness of a paper is made to be impaired. Although a paper bulking promoter containing a certain alcohol and/or a polyoxyalkylene adduct thereof was also disclosed (WO98/03730), it may be associated with an insufficiency in exerting the effect of a
15 sizing agent employed generally in combination. Furthermore, a bulking promoter, which is a fatty acid polyamide polyamine, is an available commercially, but has only a limited performance.

Disclosure of the Invention

- 20 [0003] An object of the present invention is to provide a paper bulking promoter by which sufficient bulking effect can be obtained even when the bulking promoter is added in a small amount and which does further not reduce the performance of a sizing agent added in paper-preparing step.
[0004] Thus, the invention provides a paper bulking promoter comprising an ester compound having the melting point of not more than 100°C selected from (A) an ester compound of a polyhydric alcohol and a fatty acid and (B) an
25 ester compound of a polyhydric alcohol and a fatty acid further including from more than 0 mole to less than 12 moles on the average of C₂₋₄ alkylene oxide (hereinafter referred as OA) groups per 1 mole of the said ester compound.

Industrial Applicability

- 30 [0005] According to the paper bulking promoter of the present invention, an excellent bulking effect can be obtained even when the paper bulking promoter is added in a small amount, and a bulky sheet can be obtained without impairing an effect of a sizing agent.

Mode for Carrying Out the Invention

- 35 [0006] An ester compound of the paper bulking promoter in the present invention is:
(A) an ester compound of a polyhydric alcohol and a fatty acid (an ester compound having no OA group) having the melting point of not more than 100°C, or,
40 (B) an ester compound of a polyhydric alcohol and a fatty acid, further including from more than 0 mole to less than 12 moles on the average of C₂₋₄ OA groups per 1 mole of the said ester compound and having the melting point of not more than 100°C.

- [0007] Both members as (A) and (B) of these esters may be used in combination, and two or more of each member
45 of esters may also be used.

- [0008] A polyhydric alcohol as a constituent of an ester compound in the present invention is preferably a 2- to 14-hydric alcohol having 2 to 24 carbon atoms in total which may contain an ether group. A 2- hydric (dihydric) alcohol maybe one which has 2 to 10 carbon atoms in total and which may contain an ether group, such as propylene glycol, dipropylene glycol, butylene glycol, dibutylene glycol, ethylene glycol, diethylene glycol and polyethylene glycol. Then,
50 3- (tri) or more hydric alcohol may be one which has 3 to 24 carbon atoms in total, which may contain an ether group and wherein the total number of hydroxy group/the total number of carbon atoms = 0.4 to 1 in one molecule, such as glycerol, poly(n=2 to 5)glycerol, pentaerythritol, dipentaerythritol, arabitol, sorbitol, stachyose, erythrite, arabite, mannite, glucose and sucrose. Preferably, there are ethylene glycol, diethylene glycol, propylene glycol, and an alcohol which has 3 to 12 carbon atoms in total, which may contain an ether group, wherein the total number of hydroxy
55 group/the total number of carbon atoms = 0.5 to 1 in one molecule, and which is 3- or more hydric alcohol. More preferably, there are glycerol, poly (n=2 to 4) glycerol and pentaerythritol.

- [0009] Further, a fatty acid constituting an ester compound of the present invention may be a fatty acid having 1 to 24 carbon atoms, preferably 10 to 22 carbon atoms. It may be any one of saturated, unsaturated, liner and branched

one. A linear saturated fatty acid is particularly preferable. More preferably, there are lauric acid, stearic acid, palmitic acid, myristic acid and behenic acid.

[0010] The ester compound of the present invention may be obtained by carrying out of conventionally known esterification and adding of alkylene oxide. For example, a mixture of a fatty acid and a polyhydric alcohol is, if necessary, admixed with an esterification catalyst and reacted at 150 to 250°C to obtain an ester compound (A), to which an alkylene oxide is added in the presence of an alkaline catalyst, whereby obtaining an alkylene oxide adduct (B). Alternatively, an esterification reaction may be carried out, after an alkylene oxide is added to a fatty acid or a polyhydric alcohol. Furthermore, it can be sometimes obtained by only adding an alkylene oxide to a fatty acid, too.

[0011] The average esterification degree of an ester compound in the present invention is more than 0. Preferably, per 1 mole of a polyhydric alcohol, OH in the alcohol has been esterified in an amount of 10 to 95% by equivalent. An alcohol has particularly preferably 1 to 2 moles of a fatty acid group per 1 mole of polyhydric alcohol.

[0012] When an ester compound (B) containing an OA group having 2 to 4 carbon atoms is used as a paper bulking promoter of the present invention, the number thereof (OA group) is on the average from more than 0 to less than 12 moles, preferably not more than 6 moles, and actually preferably 0.1 to 6 moles, per 1 mole of the ester compound. When a polyhydric alcohol, which can become an OA group, such as ethylene glycol, is used, the mole numbers thereof are also counted as the number of OA groups. An OA group is formed by adding an alkylene oxide having 2 to 4 carbon atoms. A preferred alkylene oxide is ethylene oxide (EO) or propylene oxide (PO). These may be used as any one of EO, PO and a mixture of EO and PO. In the present invention, it is particularly preferable to use an ester compound containing no OA group as a paper bulking promoter.

[0013] An ester compound of the present invention has HLB of preferably 1 to 14, more preferably 1.5 to 10, further preferably 2 to 8. HLB is an index for the hydrophilicity of a surfactant. The larger the value of HLB is, the higher the hydrophilicity becomes. In the present invention, the HLB of each compound is calculated by the following formula according to Griffin's method.

$$\text{HLB} = \frac{\text{Molecular weight of hydrophilic group moiety}}{\text{Molecular weight of ester compound}} \times 20$$

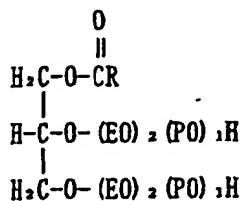
[0014] And, in the present invention, a hydrophilic group means the following group in an ester compound.

(1) $-(\text{CH}_2\text{CH}_2\text{O})_m-$

(2) $-(\text{RO})_n-$ [R: alkylene group having 3 to 4 carbon atoms, $n < 2.0$, wherein n is a total number in one molecule]

For example, the underlined part in $\text{RCOO}-(\text{PO})_{1.5}\text{H}$ represents a hydrophilic group. On the other hand, the underlined part in $\text{RCOO}-(\text{PO})_{2.0}\text{H}$ represents a hydrophobic group.

Further, in the case of the following formula:



any PO group is a hydrophobic group since one molecule contains 2 moles of PO in total.

(3) A group derived from an alcohol which may have an ether group, which is a 3- or more hydric alcohol having 3 to 24 carbon atoms in total, and wherein the total number of hydroxy group/the total number of carbon atoms = 0.4 to 1 in one molecule.

(4) An oxygen atom adjacent to a carbonyl group.

[0015] An ester compound of the present invention has the melting point of 100°C or lower, preferably -15°C or higher and 80°C or lower, more preferably 20°C or higher and 70°C or lower, from the viewpoint of handleability and preserving a sizing performance. The melting point is made to be a temperature of peak beginning, when a solid ester compound pre-cooled is measured (temperature raising ratio of 2°C/minute) by a differential scanning calorimeter (DSC).

[0016] An ester compound of the present invention is preferably one having HLB of 2 to 8 and the melting point of 10 to 70°C, and more preferably one having HLB of 2 to 7 and the melting point of 45 to 70°C. Within such range, more

preferable results of the bulk promoting effect and the sizing effect (maintained effect of a sizing agent) can be obtained.

[0017] A paper bulking promoter of the present invention is added at any step of papermaking. When it is a liquid product, it may be added as it is. Then, when it is a solid product, it may be added after pulverizing, fusing by heat or diluting with water etc. Further, if necessary, a nonionic, anionic, cationic and polymeric surfactant, and preferably a nonionic surfactant, may be used as an emulsifier or dispersant. In such case, the ratio of a paper bulking promoter in the present invention and a surfactant is: [a paper bulking promoter of the present invention]/surfactant = 99.5/0.5 to 70/30 (by weight), preferably 98/2 to 80/20.

[0018] The bulking promoter of the present invention is applicable to a variety of ordinary pulp feedstocks ranging from virgin pulps such as mechanical pulps including TMP (thermomechanical pulp) and chemical pulps including LBKP (bleached hardwood pulp) to pulps prepared from various waste papers. The point where the bulking promoter of the present invention is added is not particularly limited as long as it is within the papermaking step. The papermaking step is to form paper layers by draining water from a diluted liquid of a pulp feedstock throughout the advance thereof on a wire netting. In a factory, for example, the bulking promoter is desirably added at a point where it can be evenly blended with a pulp feedstock, such as, refiner, machine chest, or headbox. After the bulking promoter of this invention is added to a pulp feedstock, the resultant mixture is subjected as it is to sheet forming. The bulking promoter remains in the paper. The paper bulking promoter of this invention is added in an amount of 0.01 to 10 % by weight, preferably 0.1 to 5 % by weight, based on the pulp feedstock. But, in the case of some system, an excellent bulking effect can be obtained by adding a small amount of 0.1 to 1 % by weight.

[0019] The pulp sheet obtained by using the paper bulking promoter of the present invention has a bulk density (the measurement method is shown in the Examples given later) lower by preferably at least 5%, more preferably at least 7%, than the product not containing the paper bulking promoter.

[0020] At the time of papermaking, it is allowable to add a sizing agent such as a rosin, an alkyl ketene dimer, gelatin, starch and latex, moreover a filler, a yield improver, a drainability improver, a paper strength improver, and the like. A sizing agent fills voids on the surface or bulk of the paper with a water-proof material to suppress the permeation of water or inks, and can be used for paper-treatment by adding to a pulp slurry (inner sizing) or coating onto a resultant paper (surface sizing). A sizing agent is added usually in an amount of 0.01 to 1.0 % by weight based on a pulp feedstock, although the amount may vary depending on the types of the paper. Since a paper bulking promoter of the present invention is excellent also in preserving a sizing performance, it is applied preferably to a method for producing an obtainable highly bulky pulp sheet using a sizing agent in combination.

Examples

Examples 1 to 22 and Comparative Examples 1 to 9

[Pulp feedstock]

[0021] The deinked pulp and the virgin pulp shown below were used as pulp feedstocks.

(Deinked pulp)

[0022] A deinked pulp was obtained in the following manner. To feedstock waste papers collected in the city (news-paper/leaflet = 70/30%) were added warm water, 1% (based on the feedstock) of sodium hydroxide (based by weight, this is true hereinafter), 3% (based on the feedstock) of sodium silicate, 3% (based on the feedstock) of a 30% aqueous hydrogen peroxide solution, and 0.3% (based on the feedstock) of EO/PO block adduct of beef tallow/glycerol (1:1), as a deinking agent, in which the amounts of EO and PO were respectively 70 and 10 (average number of moles added). The feedstock was brushed out and then subjected to flotation. The resultant slurry was washed with water and regulated to a concentration of 1% to prepare a deinked pulp slurry. This had a freeness of 220 ml.

(Virgin pulp)

[0023] A virgin pulp was prepared by brushing out and beating an LBKP (bleached hardwood pulp) with a beater at room temperature to give a 1% LBKP slurry. This had a freeness of 420 ml.

[Papermaking method]

[0024] Each of the above 1 % pulp slurries was weighed out in such an amount as to result in a sheet of paper having a basis weight of 60 g/m². The pH thereof was adjusted to 4.5 with aluminum sulfate. Subsequently, various bulking promoters shown in Table 1 and 2 were added in amount of 0.8% based on the pulp, besides rosin sizes as sizing agent

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were added in amount of 0.5% based on the pulp. Each resultant mixture was stirred, and was formed into a sheet with a rectangular TAPPI paper machine using an 80-mesh wire. The sheet obtained was pressed with a press at 3.5 kg/cm² for 2 minutes and dried with a drum dryer at 105°C for 1 minute. After each dried sheet was held the conditions of 20°C and a humidity of 65% for 1 day to regulate its moisture content, it was evaluated for bulk density and sizing degree by the following methods. The found value was an average of 10 measurements. The results are shown in Table 3.

(Evaluation item and method)

• Bulkiness (bulk density)

[0025] The basis weight (g/m²) and thickness (mm) of each sheet having a regulated moisture content were measured, and its bulk density (g/cm³) was determined by the following calculation.

[0026] Equation for calculation:

$$\text{Bulkiness (bulk density)} = (\text{basis weight})/(\text{thickness}) \times 0.001$$

[0027] The smaller the absolute value of bulk density is, the higher the bulkiness is. A difference of 0.02 in bulk density is sufficiently recognized as a significant difference.

• Sizing-ability

[0028] The sizing performance was evaluated as directed in JIS P 8122-54 using Stöckigt sizing degree determination method. Thus, a 2 cm × 2 cm test piece of a paper obtained after the sheet formation process was floated on a 2 % solution of ammonium thiocyanate at 20±1°C contained in a petri dish and treated with dropwise addition of a 1 % solution of ferric chloride at the same temperature using a pipette, and the time period until three red spots appeared on the test piece was determined as the number of seconds, which represented the sizing degree. It is advantageous industrially to keep the sizing degree of 80 % of that of a blank (Comparative 1) or higher.

Table 1

		Paper bulking promoter				
		Ester compound	AO type and number of moles added	AO of addition form	HLB	Melting point (°C)
Examples	1	Ethylene glycol monolaurate	—	—	5.0	-2
	2	Stearic acid monoglyceride	—	—	5.1	66
	3	Pentaerythritol monostearate	—	—	6.7	52
	4	Propylene glycol sesquipalmitate	—	—	3.7	41
	5	Sorbitan monomyristate	—	—	8.7	30
	6	Arabitol dioleate	—	—	4.4	25
	7	Sorbitol trilaurate	—	—	4.9	11
	8	Saccharose monooleate	—	—	11.3	59
	9	Ethylene glycol monobehenate	—	—	3.2	64
	10	Diglycerol monomyristate	—	—	8.8	52
	11	Dipentaerythritol dipalmitate	—	—	6.9	49
	12	Triglycerol sesquioleate	—	—	7.8	12
	13	Tetraglycerol monostearate	—	—	10.8	61
	14	Ethylene glycol monooleate	EO 1 mole	—	5.7	-3
	15	Lauric acid monoglyceride	PO 0.4 mole	—	7.7	45
	16	Pentaerythritol monomyristate	EO 2 moles PO 2 moles	Block	8.1	18
	17	Propylene glycol monopalmitate	EO 1.5 moles PO 4 moles	Random	4.6	13
	18	Sorbitan monolaurate	EO 6 moles	—	14.0	-4
	19	Xylitol monostearate	PO 2 moles	—	5.7	41
	20	Mannitol sesquioleate	EO 6 moles PO 4 moles	Block	8.4	5
	21	Diethylene glycol monodecylate	EO 2 moles PO 5 moles	Random	6.0	-1
	22	Emulsified product of Example 3	—	—	—	—

[0029] The molar number of AO (Alkylene Oxide) added is an average number of AO moles added per 1 mole of an ester compound.

[0030] In the case of block addition, addition is conducted with EO and then with PO.

(Note) The composition of Example 22 represents a 10 % emulsion of Example 3/Polyoxyethylene (average number of EO moles added: 10) sorbitan monolaurate =95/5 (by weight).

Table 2

		Paper bulking promoter				
		Ester compound	AO type and number of moles added	AO addition form	HLB	Melting point (°C)
Comparative Examples	1	Blank (containing no bulking promoter)	—	—	—	—
	2	Lauryl alcohol	EO 3 moles PO 1 mole	Block	11.0	5
	3	C ₁₂₋₁₃ oxoalcohol	EO 1.5 moles	—	6.4	-2
	4	80/20 (by weight) mixture of decyl alcohol/30 moles of EO adduct to sorbitan trioleate	—	—	4.3	2
	5	Sorbitol tetraoleate	EO 30 moles	—	11.7	-10
	6	Sorbitan monopalmitate	EO 20 moles	—	16.3	-14
	7	Commercial bulking promoter "Bayvolume P Liquid" (fatty acid polyamide polyamine type; manufactured by Bayer AG)	—	—	—	—
	8	Sorbitan monooleate	EO 12 moles	—	14.5	-5
	9	Distearyl phthalate	—	—	1.0	45

[0031] The number of AO (Alkylene Oxide) moles added is an average number of added moles per 1 mole of monomer ester.

[0032] In the case of block addition, addition is conducted with EO, and then with PO.

Table 3

		Deinked pulp		LBKP	
		Bulk density (g/cm ³)	Sizing degree (second)	Bulk density (g/cm ³)	Sizing degree (second)
Examples	1	0.339	58	0.382	66
	2	0.315	73	0.361	82
	3	0.313	72	0.360	82
	4	0.327	67	0.372	76
	5	0.330	64	0.376	72
	6	0.331	63	0.377	71
	7	0.335	61	0.377	67
	8	0.326	70	0.369	78
	9	0.318	72	0.362	82
	10	0.320	71	0.364	81
	11	0.324	69	0.367	78
	12	0.336	62	0.378	67
	13	0.317	72	0.363	81
	14	0.340	57	0.384	66
	15	0.322	69	0.366	78
	16	0.338	62	0.380	70
	17	0.337	62	0.379	69
	18	0.344	56	0.388	65
	19	0.328	68	0.373	76
	20	0.339	59	0.383	68
	21	0.341	57	0.385	67
	22	0.313	71	0.360	82
Comparative examples	1	0.376	70	0.413	80
	2	0.362	0	0.404	0
	3	0.362	9	0.405	10
	4	0.365	0	0.406	0
	5	0.367	0	0.407	0
	6	0.363	0	0.404	0
	7	0.372	0	0.411	0
	8	0.360	8	0.403	10
	9	0.373	15	0.412	17

Claims

1. A paper bulking promoter comprising an ester compound having the melting point of not more than 100°C, selected from (A) an ester compound of a polyhydric alcohol and a fatty acid and (B) an ester compound of a polyhydric alcohol and a fatty acid further including from more than 0 mole to less than 12 moles on the average of C₂₋₄ oxyalkylene groups per 1 mole of the said ester compound.
2. The paper bulking promoter as claimed in Claim 1 wherein the polyhydric alcohol is a 2- to 14- hydric alcohol having

2 to 24 carbon atoms in total which may contain an ether group.

3. The paper bulking promoter as claimed in Claim 1 or 2 wherein the fatty acid is a fatty acid having 1 to 24 carbon atoms.
4. The paper bulking promoter as claimed in any one of Claims 1 to 3 wherein the ester compound contains no oxy-alkylene group.
5. The paper bulking promoter as claimed in Claim 1 wherein 10 to 95 % by equivalent of OH groups of the alcohol have been esterified.
6. A method for producing a highly bulky pulp sheet wherein a paper bulking promoter as defined in any one of Claims 1 to 4 is added at any step of papermaking process.
7. A method as claimed in Claim 5 wherein a sizing agent is further added at any step of papermaking process.
8. A highly bulky pulp sheet produced by adding a paper bulking promoter as defined in any one of Claims 1 to 4 at any step of papermaking process.
9. Use, as a paper bulking promoter, of an ester compound having the melting point of not more than 100°C selected from (A) an ester compound of a polyhydric alcohol and a fatty acid and (B) an ester compound of a polyhydric alcohol and a fatty acid and further including from more than 0 mole to less than 12 moles on the average of C₂₋₄ oxy-alkylene groups per 1 mole of the said ester compound.
10. A method for producing a highly bulky pulp sheet comprising adding a paper bulking promoter as defined in any one of Claims 1 to 4, another sizing agent and a surfactant at any step of papermaking process.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/02947

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ D21H17/14, D21H21/24 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ D21H17/14, D21H21/22-24 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 57-101096, A (Kao Soap Co., Ltd.), 23 June, 1982 (23. 06. 82), Full text (Family: none)	6-8, 10
A	Full text (Family: none)	1-5, 9
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 6 August, 1999 (06. 08. 99)		Date of mailing of the international search report 17 August, 1999 (17. 08. 99)
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